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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR PREPARING BARIUM-TITANATE BASED POWDER

(57) Abstract: The present invention relates to a method for preparing barium titanate based powder. More particularly, the present invention provides a method for preparing barium titanate powder comprising the following steps of precipitation of barium tityl oxalate ($\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$) with spraying a mixture of an aqueous barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and titanium tetrachloride (TiCl_4) to an aqueous solution of oxalic acid, via a nozzle; wet pulverization by using a beads mill after adding an additive such as an amine; dry; pyrolysis; and re-pulverization.



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METHOD FOR PREPARING BARIUM-TITANATE BASED POWDER

FIELD OF INVENTION

The present invention relates to a method for preparing barium titanate based powder. More particularly, the present invention provides a method for preparing barium titanate powder comprising the following steps of : precipitating barium titanyl oxalate ($\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$) by spraying an aqueous mixture of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and titanium tetrachloride (TiCl_4) to an aqueous solution of oxalic acid, via a nozzle; wet pulverization by using a beads mill after adding an additive such as an amine; drying; pyrolysis; and re-pulverization.

BACKGROUND OF THE INVENTION

The barium titanate powder has been widely utilized to produce multi-layer ceramic chip capacitors (MLCC), positive temperature coefficient thermistors, resistors, and the like. It is well-known that barium titanate powder can be manufactured via solid state reaction of barium carbonate (BaCO_3) and titanium dioxide (TiO_2) at high temperature. As the trend in MLCC (multi-layer ceramic chip capacitor) continues towards further and further miniaturization with large capacity, calcination at a low temperature, high frequency, and volumetric efficiency, the demand for not only finer and more uniform barium titanate powders has increased tremendously, but the need for purity and distribution has also escalated as well. Thus, various liquid state reaction methods such as hydrothermal method, co-precipitation

(oxalate) method, and alkoxide method have been developed to produce barium titanate powders satisfying these characteristics.

The oxalate method is well discussed by W. S. Clabaugh et al. in *Journal of Research of the National Bureau of Standards*, Vol. 56(5), 289-291(1956) to
5 produce barium titanate by precipitating barium titanyl oxalate with addition of a mixture solution containing Ba and Ti ions to an oxalic acid. However, this method has several drawbacks: (i) it is difficult to control particle size and stoichiometric mole ratio of Ba to Ti; (ii) hard aggregates between particles are formed during the pyrolysis, thus requiring strong pulverization to remove
10 these hard aggregates; (iii) because extremely fine particles are enormously produced during the strong pulverizing, it is hard to disperse the powder for forming and abnormal grain growth occur during sintering process. Thus, the barium titanate powders produced in this manner are not adequate for the applications to multilayer ceramic capacitors.

15 Therefore, a hydrothermal method has been recently given attention to because of the trend of thinner and higher layered dielectric layer in MLCC. However, This method has disadvantages, like high manufacturing cost and complex process, due to use of autoclave, in spite of its high product quality. Therefore, there are increasing demands for developing simpler methods for
20 preparing barium titanate powders in low price to be competitive in the market.

Inventors of the present invention have filed patent applications in South Korea (Korea Patent Application Nos. 2000-46125 and 2001-9066) for the preparation of barium titanate powder which exhibit improved yield with shortened reaction time and optimized stoichiometry of barium to titanium.

The method for preparing barium titanate powder disclosed in the above Korea Patent applications comprises the steps of: precipitating barium titanyl oxalate ($\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$) by spraying an aqueous mixture of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and titanium tetrachloride (TiCl_4) to an aqueous solution of oxalic acid, via a nozzle in high speed and aging, filtering and washing the same; pulverizing the obtained barium titanyl oxalate, drying, and pyrolyzing to produce barium titanate (BaTiO_3) powder; and re-pulverizing the pre-pulverized barium titanate powder. In the pulverizing process, it can be performed by methods such as dry pulverization using an atomizer and jet mill or wet pulverization using a ball mill, planetary mill, and beads mill. In case it is needed to blend barium titanate (BaTiO_3) with other metal additives in the pulverizing step, wet pulverization is more preferable. Among wet pulverizing instruments, planetary mill or ball mill is suitable for laboratory scale, while a beads mill is for industrial scale.

However, when the beads mill is employed for the wet pulverization of barium titanyl oxalate it causes the following problems:

(1) Impurities present in the solution occlude inside barium titanyl oxalate particles during the precipitating step. Thus, impurities, such as oxalic acid or chloride ion remain in barium titanyl oxalate prepared by co-precipitation (oxalate) method, no matter how many it is washed. Since this barium titanyl oxalate mixed with water has pH around 3, it may cause corrosion of pre-mixer whose material is stainless steel. Further, it is difficult to control exothermic heat in case of using acid-resistant material such as polyurethane. Therefore, it requires a use of expensive material like titanium

as a pre-mixer. After the wet pulverization, the pH of the barium titanyl oxalate slurry becomes 2 which is lower than that before the wet pulverization. Thus, it may decrease material's durability of beads mill(inside part of mill chamber) like zirconia and polyurethane. Furthermore it causes corrosion of a
5 dryer.

(2) The presence of chloride ions in the barium titanyl oxalate will result in the formation of a BaCl_2 liquid phase during sintering, which is disclosed in *Journal of Inorganic chemistry*, vol. 9(11) 2381~89(1970). Thus, the calcined barium titanate aggregates more and exhibits poor dielectric characteristics.

10

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a process for producing barium titanate powder economically by solving problems associated with the wet pulverization of barium titanyl oxalate in the process
15 for preparing barium titanate disclosed in Korea Patent Nos. 2000-46125 and 2001-9066.

BRIEF DESCRIPTION OF DRAWING

The above object of the present invention will become apparent from the
20 following description of the invention, when taken in conjunction with the accompanying drawing, in which:

FIG. 1 represents SEM image of barium titanate powder produced by the method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method for preparing barium titanate powder comprising the steps of:

precipitating barium titanyl oxalate ($\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$) by spraying
5 an aqueous mixture of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and titanium tetrachloride (TiCl_4) to an aqueous solution of oxalic acid, via a nozzle;

wet pulverization by using a beads mill after adding an additive chosen from ammonia, amine, ammonium compound and amino acid;

pyrolyzing to produce barium titanate powder; and
10 re-pulverization the obtained barium titanate powder.

The present invention will become apparent from the following description of the invention, when the process for preparing barium titanate powder is described in more detail.

The first step is precipitation of barium titanyl oxalate with spraying an
15 aqueous mixture of barium chloride and titanium tetrachloride to an aqueous solution of oxalic acid via a nozzle in high speed, aging, filtration, and washing with water. The aqueous barium chloride solution is prepared by dissolving barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water, and preferable barium chloride concentration is in the range of from 0.2 to 2.0 mol/l. The aqueous
20 titanium tetrachloride solution is prepared by diluting titanium tetrachloride solution, and preferable titanium tetrachloride concentration is in the range of from 0.2 to 2.0 mol/l. The mole ratio of the barium compound / titanium compound is controlled being in the range of from 1 to 1.5, more preferably 1 to 1.1 when the aqueous solutions of barium chloride and titanium tetrachloride

are added each other. A concentration of the aqueous oxalic acid solution is preferably in the range of from 0.2 to 5.0 mol/l and a temperature is maintained in the range of 20 to 100 °C, more preferably 50 to 90 °C.

The prepared mixture of barium chloride and titanium tetrachloride is
5 added by spraying into an aqueous oxalic acid solution for 1 t o 3 hours through a nozzle. The nozzle used in the present invention may be a single-fluid nozzle or double-fluid, preferably single-fluid nozzle as a matter of convenience.

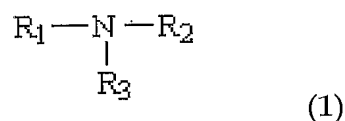
The aging is performed for 0.5 to 2 hours and then the crude barium
10 titanyl oxalate is washed with water till pH of the washer turns to neutral to produce the corresponding barium titanyl oxalate.

The second step is wet pulverization of the obtained barium titanyl oxalate by means of a beads mill and drying. A solvent used for the wet pulverization is deionized water of which amount used is 1 to 10 parts by
15 weight, relative to 1 part by weight of barium titanyl oxalate. During the process of the wet pulverization, a nitrogen-containing additive is added to prevent from acidification of the mixture after pulverization and decrease of dielectric characteristics of the powder due to the presence of chloride ions within the barium titanyl oxalate.

20 Examples of the nitrogen-containing additive include ammonia, amines, ammonium compounds and amino acids. Particularly, use of an inorganic base such as sodium hydroxide, potassium carbonate and sodium bicarbonate is not preferable to remove chloride ions due to decrease of dielectric characteristics of the powder such as dielectric constant and insulation

resistance. However, the nitrogen-containing additive used in the present invention is preferable due to no containing of metal cations.

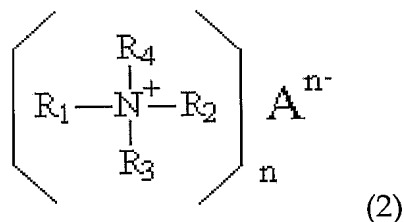
The amine used in the present invention is expressed by the following formula (1),



wherein R_1 , R_2 , and R_3 represent individually hydrogen atom or C_1 - C_5 alkyl.

Examples of primary, secondary or tertiary amine include methylamine, dimethylamine, trimethylamine, diethylamine and triethylamine.

The ammonium compound used in the present invention is expressed by the following formula (2),



wherein R_1 , R_2 , and R_3 represent individually hydrogen atom or C_1 - C_5 alkyl; A represents hydroxyl ($n=1$), nitrate ($n=1$), sulfate ($n=2$), phosphate ($n=3$), carbonate ($n=2$), bicarbonate ($n=1$), C_1 - C_{10} carboxyl ($n=1$), or C_2 - C_{10} dicarboxyl group ($n=2$).

Preferred examples of the ammonium compound include ammonium hydroxide, ammonium carbonate, ammonium acetate, ammonium phosphate, ammonium oxalate, ammonium bicarbonate, and trimethylammonium hydroxide. Examples of the amino acid include arginine and lysine.

The nitrogen-containing additive is used in the range of from 0.5 to 20 mol%. If it is less than 0.5 mol%, it is undesirable in acidity and chloride content of the slurry. On the other hand, if it exceeds 20 mol%, it results in non-stoichiometric mole ratio of Ba to Ti due to loss of titanium component.

5 Further, a divalent or tetravalent metal may be arbitrarily incorporated with the nitrogen-containing additive and replaced for Ba or Ti position. A divalent metal may be replaced for Ba and a tetravalent metal may be for Ti. Examples of the divalent metal include Mg, Ca, Sr, and Pb and those of the tetravalent element include Zr, Hf, and Sn. These metals may be used in the
10 form of oxides, carbonates, chlorides or nitrates. For example, an oxide, carbonate, chloride or nitrate of such a replacement element is added to the barium titanyl oxalate to produce perovskite-type barium titanate based powder such as $\text{Ba}(\text{Ti}_{1-z}\text{Zr}_z)\text{O}_3$, $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{1-z}\text{Zr}_z)\text{O}_3$, $(\text{Ba}_{1-x-y}\text{Ca}_x\text{Sr}_y)(\text{Ti}_{1-z}\text{Zr}_z)\text{O}_3$, and the like.

15 The wet pulverized barium titanyl oxalate is dried and pyrolyzed to form barium titanate in the presence of the additive. A rate for heating during the pyrolysis is preferably in the range of 0.5 to 10 °C/min and a temperature is maintained at 700 to 1200 °C.

The last step is re-pulverization of the obtained barium titanate powder.
20 The barium titanate powder can be easily pulverized by means of dry pulverization using an atomizer, or jet mill or wet pulverization using a ball mill, planetary mill, or beads mill. Drying is performed using oven, dryer, or spray dryer only when the wet pulverization is carried.

The following examples are intended to further illustrate the present

invention without limiting its scope. Further, the scope of the present invention is not limited to barium titanate powder but includes potential barium titanate-based powders depending on kinds and contents of additives added.

5

Example 1

1200 l of an aqueous 1 mol/l TiCl_4 and 1320 l of an aqueous 1 mol/l BaCl_2 were added to a glass-lined 4 M³ reactor and mixed. The mixture was sprayed to 2520 l of an aqueous 1 mol/l oxalic acid in 6 M³ reactor through a
10 single-fluid nozzle such as full-con at a rate of 21 l/min. The oxalic acid solution was stirred with a rate of 150 rpm and a temperature was maintained at 90 °C. A diaphragm pump was used as a supplying pump for spraying the mixture solution. After spraying the mixture to an oxalic acid for 2 hours, the mixture solution was stirred at a reaction temperature for 1 hour and at room
15 temperature for 1 hour to produce barium titanyl oxalate slurry. The barium titanyl oxalate slurry was filtered using a centrifuge and washed with water till pH of the filtrate turned to above pH 6. Yield was 98% based on Ti ion and a mole ratio of Ba to Ti was 0.999 (water content of 24%).

0.5 kg of 29 wt.% aqueous ammonia (10.1 mol%, relative to the barium
20 titanyl oxalate) was added to 50 kg of the barium titanyl oxalate in 250 kg of deionized water. The slurry was stirred and the pH thereof before the pulverization was 9.3. Then, the slurry was performed for the wet pulverization to be 15 µm of maximum particle size with a beads mill. The pH of the slurry after the pulverization was 5.1. After the obtained barium titanyl

oxalate slurry was dried in an oven at 120 °C for 12 hours, the chloride ion content was 200 ppm. The barium titanyl oxalate slurry was then pyrolyzed at 1200 °C in an electric furnace and performed for dry-pulverization to produce barium titanate powder. SEM image of barium titanate powder was
5 represented in Fig. 1.

Examples 2-6

Barium titanate powder was prepared by the same procedure as in Example 1, except varying amount of aqueous ammonia during the wet
10 pulverization. The characteristics of the obtained slurry were summarized in Table 1.

Comparative Example 1

Barium titanyl oxalate was prepared by the same procedure as in
15 Example 1 and the mole ratio of Ba/Ti was 0.999 (water content of 24%).

50 kg of the barium titanyl oxalate and 250 kg of deionized water were placed and stirred in the reactor. The pH of the slurry before the pulverization was 3.0. Then, the slurry was performed for the wet pulverization to be 15 µm of maximum particle size with a beads mill. The pH of the slurry after the
20 pulverization was 2.0. After the obtained barium titanyl oxalate slurry was dried in an oven at 120 °C for 12 hours, the chloride ion content was 10000 ppm. Then, barium titanate powder was prepared by the same procedure as in Example 1.

Table 1

Category	Used amount of aqueous ammonia (mol%)	Before pulverization		After pulverization		
		pH	Ba/Ti ratio*	pH	Content of Cl ⁻	Ba/Ti ratio*
Exam. 1	10.1	9.3	0.999	5.1	200	0.999
Exam. 2	0.4	8.3	0.999	3.0	500	0.999
Exam. 3	0.5	9.0	0.999	5.0	200	0.999
Exam. 4	20	10.0	0.999	5.2	200	0.999
Exam. 5	21	10.2	0.999	5.4	200	1.001
Exam. 6	25	10.2	0.999	5.4	200	1.005
Com. Exam. 1	-	3.0	0.999	2.0	10000	0.999
Ba/Ti ratio*: XRF measurement						

Examples 7-12

Barium titanate powder was prepared by the same procedure as in

5 Example 1, except using different additive with different amount during the wet pulverization. The characteristics of the obtained slurry were summarized in Table 2.

Table 2

Category	Additive		Before pulverization		After pulverization		
	Additive	Amount (mol%)	pH	Ba/Ti ratio*	pH	Content of Cl ⁻	Ba/Ti ratio*
Ex. 7	Ammonium acetate	10	6.8	0.999	5.1	200	0.999
Ex. 8	Ammonium nitrate	8	5.5	0.999	4.9	200	0.999
Ex. 9	triethylamine	15	10.2	0.999	5.0	200	0.999
Ex. 10	Ammonium carbonate	14	7.9	0.999	4.8	200	0.999
Ex. 11	Ammonium phosphate	13	8.1	0.999	5.0	200	0.999
Ex. 12	arginine	12	8.0	0.999	4.8	200	0.999
Ba/Ti ratio*: XRF measurement							

Example 13

Barium titanyl oxalate was prepared by the same procedure as in
 5 Example 1, except addition of aqueous ammonia and additionally CaCO_3 and ZrO_2 during the pulverization process. Then it was performed for dry, pyrolysis at 1190 °C, and pulverization to produce $(\text{Ba}_{0.952}\text{Ca}_{0.05})(\text{Ti}_{0.84}\text{Zr}_{0.16})\text{O}_3$.

The obtained perovskite barium titanate powder has 0.52 μm of average particle size and 4.02 m^2/g of specific surface.

10

Comparative Example 2

$(\text{Ba}_{0.952}\text{Ca}_{0.05})(\text{Ti}_{0.84}\text{Zr}_{0.16})\text{O}_3$ was prepared by the same procedure as in

Example 13, except that aqueous ammonia was not added during the pulverization process.

The obtained perovskite barium titanate powder has 0.54 μm of average particle size and 4.01 m^2/g of specific surface.

5

Experimental Example : determination of conductivity characteristics

A PVA binder and some additives for Y5V were added to each barium titanate powder prepared in Example 13 and Comparative Example 2. Each mixture was well mixed in an alumina mortar and dried. Then, each mixture was crushed in the mortar and sieved in order to obtain granules. 0.4 g of each granule was pressed into a Φ 10 mm disc in a mold. Then some dielectric characteristics were tested and the results are shown in Table 3.

Table 3

Category	Green density (g/cm^3)	Sintering density (g/cm^3)	Dielectric Constant	Dielectric loss (%)	Insulating resistance ($10^{11}\Omega$)	TCC* (%)
Ex. 13	3.69	5.90	12100	3.72	0.44	-60.3/10.2
Com. Ex. 2	3.68	5.89	10000	4.57	0.01	-67.2/13.8
* TCC: Temperature coefficient of capacitance						

15

As shown in Table 3, the barium titanate powder (Example 13) prepared by using an additive during the wet pulverization process according to the present invention has superior conductivity characteristics (e.g., higher

dielectricity, higher insulating resistance, lower dielectric loss) compared to the barium titanate powder (Comparative Example 2) prepared by the conventional method.

As described above, in the preparing process of barium titanate powder
5 of high quality employing oxalate-derived method, the present invention
provides an improved manufacturing process of the barium titanate powder by
employing a nitrogen-containing additive such as amines to barium titanyl
oxalate during the wet pulverization which prevents from the acidification of
the slurry and decreasing the dielectric characteristics of the powder before and
10 after the pulverization due to the presence of chloride ions. It is, therefore,
suitable for as materials for multilayer ceramic capacitors, PTC thermistors,
resistors, and the like.

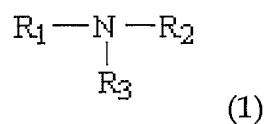
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CLAIMS

What is claimed is :

- 5 1. A method for preparing barium titanate powder comprising the steps of:
precipitating a mixture of aqueous barium chloride and titanium tetrachloride to an aqueous oxalic acid by spraying via a nozzle in high speed, aging, filtering and washing to obtain barium titanyl oxalate;
wet pulverizing the obtained barium titanyl oxalate after adding a
10 nitrogen-containing additive chosen from ammonia, amines, ammonium compound, and amino acids by means of a beads mill, drying and pyrolyzing to produce barium titanate powder; and
re-pulverizing the obtained barium titanate powder.
- 15 2. A method for preparing barium titanate powder of claim 1, wherein said nitrogen-containing additive is used in the range of 0.5 to 20 mol% relative to barium titanyl oxalate.
3. A method for preparing barium titanate powder of claim 1, wherein said
20 amine is expressed by the following formula (1),

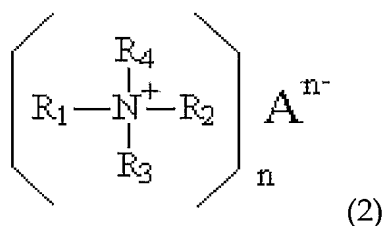


wherein R₁, R₂, and R₃ represent individually hydrogen atom or C₁-C₅ alkyl.

4. A method for preparing barium titanate powder of claim 3, wherein said amine is selected from the group consisting of methyl amine, dimethylamine, trimethylamine, diethylamine, and triethylamine.

5

5. A method for preparing barium titanate powder of claim 1, wherein said ammonium compound is expressed by the following formula (2),



wherein R₁, R₂, and R₃ represent individually hydrogen atom or C₁-C₅ alkyl; A represents hydroxyl (n=1), nitrate (n=1), sulfate (n=2), phosphate (n=3), carbonate (n=2), bicarbonate (n=1), C₁-C₁₀ carboxyl (n=1), or C₂-C₁₀ dicarboxyl group (n=2).

6. A method for preparing barium titanate powder of claim 5, wherein said ammonium compound is selected from the group consisting of ammonium hydroxide, ammonium carbonate, ammonium acetate, ammonium phosphate, ammonium oxalate, ammonium bicarbonate, and trimethylammonium hydroxide.

7. A method for preparing barium titanate powder of claim 1, wherein said amino acid is selected from the group consisting of arginine and lysine.

divalent or tetravalent metal is used with said nitrogen-containing additive.

9. A method for preparing barium titanate powder of claim 8, wherein said
divalent metal is at least one selected from the group consisting of Mg, Ca, Sr,
5 and Pb.

10. A method for preparing barium titanate powder of claim 8, wherein said
tetravalent metal is at least one selected from the group consisting of Zr, Hf,
and Sn.

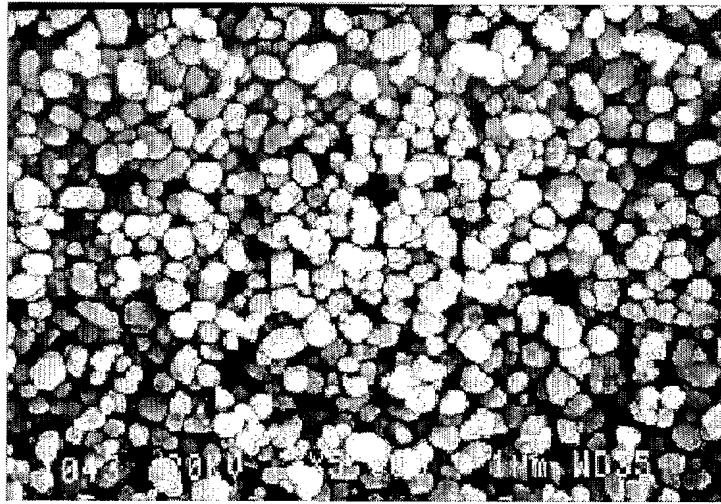
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11. A method for preparing barium titanate powder of any one of claims 8, 9,
and 10, wherein said additive is chosen from oxides, carbonates, chlorides or
nitrates of said metal.

15

20

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 02/00836

CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C01G 23/00, C01F 11/00 // C04B 35/468

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: C01G 23/00, C01F 11/00 // C08B 35/468

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AT patent documents

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI database, Derwent Publ. Ltd., CAPlus Database, STN International;

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

24 July 2002 (24.07.2002)

Date of mailing of the international search report

8 August 2002 (08.08.2002)

Name and mailing address of the ISA/AT

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 02/00836

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>C.Q. TANG et al., "The Defects, Grain Size and Electrical Property in the Non-stoichiometric BaTiO₃ Ceramics", Cryst. Res. Technol. 35, 2000, pages 609-614; <i>"Experiments and results"</i>.</p> <p>-----</p>	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 02/00836-0

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KR	A	20010088 07		none			
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				JP	B2	2558357	27-11-1996
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				EP	A1	415428	06-03-1991
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				JP	A2	4031358	03-02-1992
				JP	B2	2569205	08-01-1997
				JP	A2	4065356	02-03-1992
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